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Oxidation of unvulcanized, unstabilized polychloroprene: A kinetic study

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A B S T R A C T

Thermal oxidation in air at atmospheric pressure, in the 80–140 °C temperature range and in oxygen at 100 °C in the 0.02–3 MPa pressure range, of unvulcanized, unstabilized, unfilled polychloroprene (CR) has been characterized using FTIR and chlorine concentration measurement. The kinetic analysis was focused on double bond consumption. A mechanistic scheme involving unimolecular and bimolecular hydroperoxide decomposition, oxygen addition to alkyl radicals, hydrogen abstraction on allylic methylenes, alkyl and peroxyl additions to double bonds and terminations involving alkyl and peroxy radicals was elaborated. The corresponding rate constants were partly extracted from the literature and partly determined from experimental data using the kinetic model derived from the mechanistic scheme in an inverse approach. Among the specificities of polychloroprene, the following were revealed: The rate of double bond consumption is a hyperbolic function of oxygen pressure that allows a law previously established for the oxidation of saturated substrates to be generalized. CR oxidation is characterized by the absence of an induction period that reveals the instability of hydroperoxides. The kinetic analysis also reveals that peroxyl addition is faster than hydrogen abstraction but slower in CR than in common hydrocarbon polydienes.

1. Introduction

Elastomers derived from vulcanized poly 2 chloro butadiene (polychloroprene) have been known for almost 80 years. They show better resistance to ozone and oil than common hydrocarbon polydienic elastomers and are particularly appreciated for their good properties in aqueous media (gloves, joints, etc.). It is now well recognized that radical chain oxidation is one of the most important modes of thermal ageing for this polymer, that has led to a non-negligible amount of literature in the past half century. Despite that, certain aspects of their degradation mechanisms remain obscure and the available quantitative data remain largely insufficient to envisage non-empirical lifetime prediction based on an indisputable kinetic model. The aim of this work is to try to contribute to the elaboration of such model. It has been chosen to decompose the investigation into several steps, corresponding to material structure and composition of increasing complexity. The first step corresponds to the starting polychloroprene (lCR) linear polymer. In the industrial samples under study, all the other material components (crosslinks, fillers) are in relatively low concentration or unreactive and are thus expected to have an influence of second order on oxidation behaviour. This latter will be thus described as the oxidation of lCR monomer units (and/or structural irregularities) eventually perturbed by crosslinking agents and additives. The second step of the investigation will focus on additive-free vulcanisates (vCR) in order to appreciate the effect of crosslinking agents (here sulphur, of which the effect on oxidation has already been the object of many studies for other elastomers). The third step consists of studying the effect of stabilizers on the oxidation of industrial vulcanisates (iCR).

Concerning the relatively recent literature on polychloroprene thermal ageing, we dispose first of data relative to thermal degradation in neutral atmosphere at 150 °C [1]. NMR and IR data indicate the important role of 1–2/1–4 sequences (Fig. 1). Commercial grades of lCR are essentially composed of 1–4 sequences but some 1–2 isomers are present, and are characterized by the presence of a labile chlorine atom destabilized by its tertiary placement and by the presence of a double bond in an α position. The homolytic splitting of the C–Cl bond is favoured by the resonance stabilization of the resulting allyl radical. Cl° radicals can add to double bonds or

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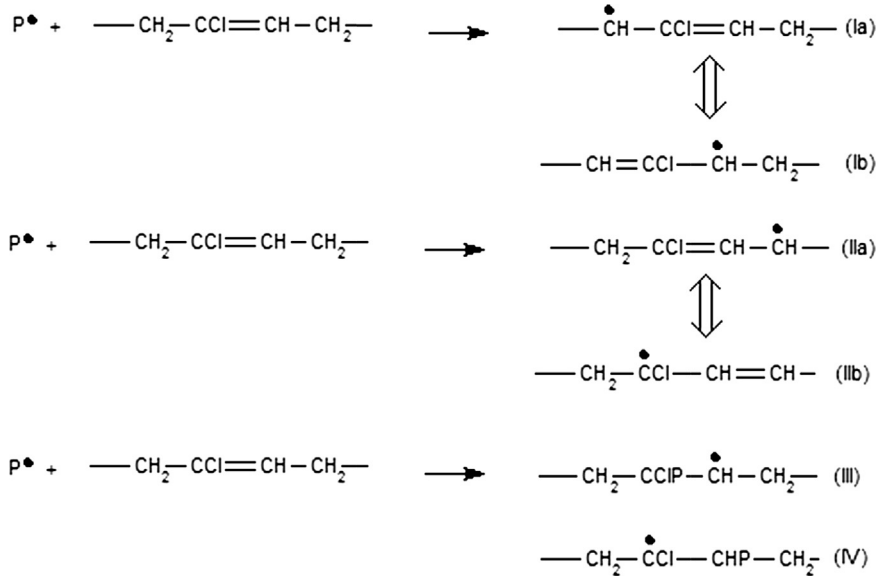

Fig. 1. Possible reactions of the 1–4 monomer unit with a radical.

abstract hydrogens to give hydrogen chloride and thus propagate oxidation. Miyata and Atsumi [1] show a correlation between the yields of 1–2 isomerizations and HCl evolution indicating that the 1–2 isomer is the precursor of both species. How to exploit these results in the frame of a study of thermal oxidation? The first approach is to suppose that oxidation radical chains could be initiated by the thermolysis of a labile polymer bond. The dissociation energy of C–Cl bonds attached to double bonds, as in the monomer unit, is very high; these bonds cannot participate in initiation events. Secondary C–Cl bonds in regular monomer units of PVC for instance have dissociation energy of 320 ± 10 kJ/mol, lower than that of C–H bonds in saturated compounds but stable at least at temperatures lower than 80 °C. Tertiary C–Cl bonds or allylic C–Cl bonds are destabilized by respectively inductive and mesomeric effects; they are often cited as "weak points" in the thermal degradation of PVC. Indeed tertiary C–Cl bonds in allylic placement, combining both destabilizing effects, must be especially unstable. Their dissociation energy is expected to be of the order of 250 kJ/mol. They can therefore play a role in initial steps of lCR or CR thermal oxidation. However, it must be recalled that oxidation leads to the formation of peroxides (including hydroperoxides) of which the dissociation energy is of the order of 180 kJ/mol in hydrocarbon peroxides and significantly lower in α chloro peroxides of which the explosive behaviour at temperatures close to ambient temperature has been the cause of major catastrophes, in PVC polymerization plants for instance.

Let us now consider thermal oxidation. A significant difficulty in the study of polydiene oxidation is the occurrence of two kinds of radical propagation processes: hydrogen abstraction on allylic carbons and addition reactions on double bonds. In the case of a dissymmetric monomer unit such as the polychloroprene one, this opens the way to at least four reaction pathways, even six if isomerizations of allyl radicals are taken into account, Fig. 1.

Let us first note that radicals Ia and Ib are identical, they will be called I here. In the following, only radical Ia will be considered. The existence of intermediary allyl radicals has been recognized for a long time [2]. According to Shelton et al. path II is favoured relative to path I [3] owing to the stabilizing effect of the chlorine atom in the β position of the reacted methylene. Concerning addition reactions, we dispose of the example of PVC polymerization [4] to appreciate the relative probability of the formation of radicals III or IV. It is clear that the "anti Markovnikov" process - in which it is the less substituted carbon which is attacked - is favoured. Additions are thus expected to give predominantly radical IV. To summarize, we expect the presence of essentially three "primary radicals": IIa, IIb and IV.

These radicals react very fast with oxygen to give considerably less reactive peroxy radicals. The latter can abstract hydrogens on allylic methylenes or add to double bonds. As in the case of polyisoprene [5], additions can be inter or intramolecular; in the first case they give crosslinks, in the second they give cycles. In the case of α chloroperoxyls, an interesting peculiarity is the possibility, for the cyclization, to propagate as a zip reaction along the chain. It is noteworthy that, except for hydroperoxides coming from radical IIa, all the other peroxides or hydroperoxides have a chlorine atom in α position. The high instability of α chloro peroxides is well known; it is presumably responsible for the absence of an induction period in lPCR oxidation. Finally, we expect for each primary radical three kinds of products: hydroperoxides, intermolecular peroxide bridges and cyclic peroxides, which may form sequences.

Highly sensitive methods for measuring oxygen absorption allowed interesting quantitative results to be obtained: values of the order of $1.3 \cdot 10^{-9}$ [6] or $3–4\ 10^{-9}$ mol kg^{-1} s^{-1} [7] have been observed at 50 °C. The measurements reveal that a steady state is established rapidly after the beginning of exposure. As frequently found, the apparent activation energy for global oxidation is higher at high temperature (typically above 80 °C) than at low temperature [6,7]. This behaviour has been explained by the fact that termination processes, which are the most dependent on segmental mobility among all the other elementary steps of oxidation radical chains, are less and less efficient when the temperature decreases [8].

The nature of stable oxidation products has been investigated by Delor et al. [9] essentially on the basis of IR measurements. As expected the spectra reveal the disappearance of double bonds and the appearance of a variety of oxygen containing structures, among which acid chlorides absorbing at 1790 cm^{-1} of which the presence has been confirmed by derivatization (transformation into primary amine by reaction with ammonia). Delor et al. proposed a mechanistic scheme for processes starting from a hydrogen abstraction event; addition processes were neglected, probably because

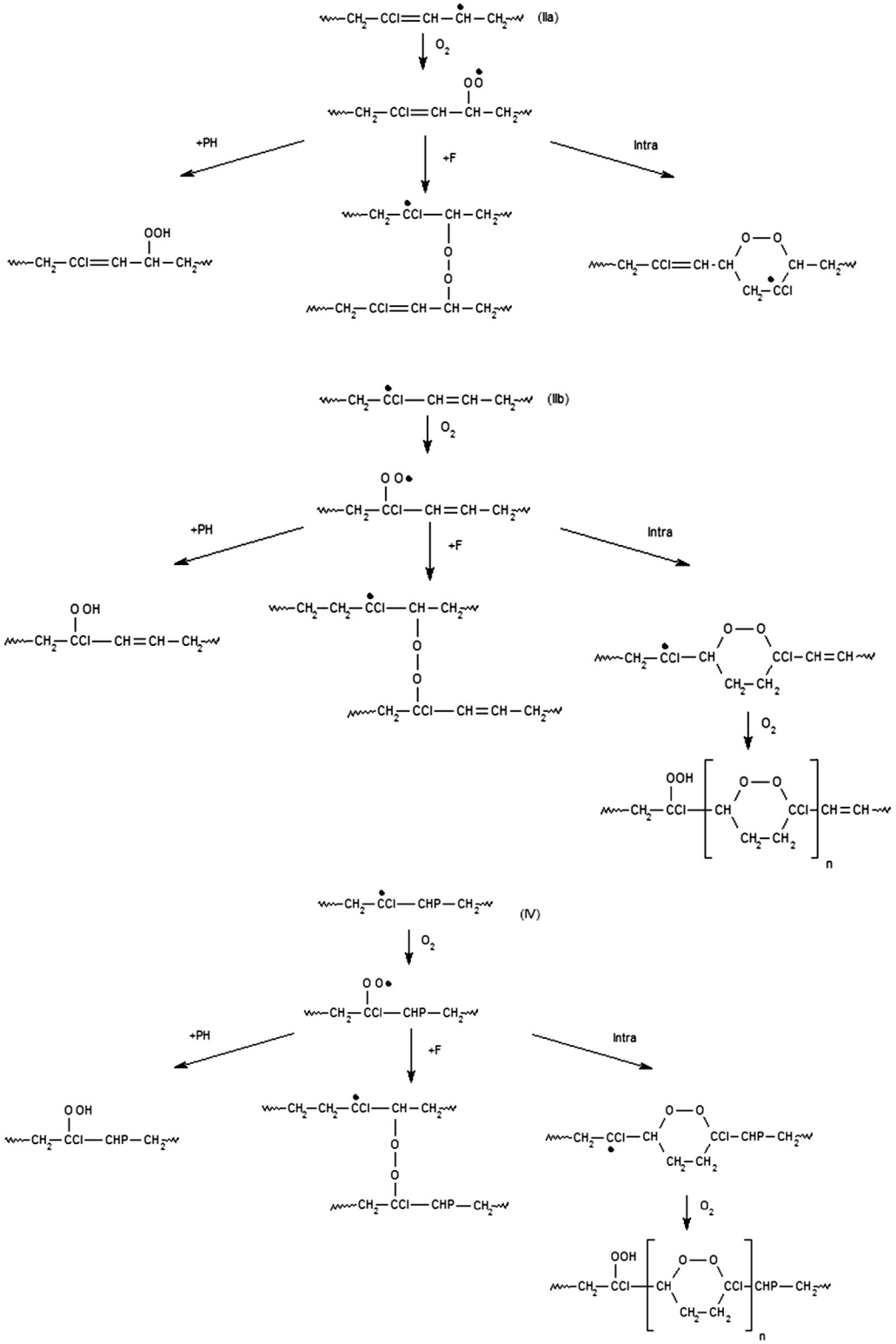

Fig. 2. Formation d'hydroperoxydes et de peroxydes à partir des principaux radicaux primaires.

peroxides resulting from these processes have very discrete IR spectra, their decomposition products are not necessarily different from those of hydroperoxides so that peroxides need often to be identified by indirect methods.

When comparing iCR with hydrocarbon polydienes, the most striking difference is, no doubt, the presence of the peak at 1790 cm^{-1} attributed to acid chlorides. It seems logical to attribute their formation, as proposed by Delor et al. [9 to the oxidative attack of the carbon bearing a chlorine atom. As previously quoted, the corresponding hydroperoxides are highly unstable, their decomposition gives an α chloroalkoxyl which, according to Delor et al. [9] would lead to the acid chloride by β scission. However

splitting of the C—Cl bond can be a competitive β scission process leading to a ketone. Anyhow, it is difficult to imagine another mechanism for acid chloride formation (Fig. 2).

Gillen et al. [6] have also measured the quantity of CO_2 evolved. The ratio CO_2 evolved/O_2 absorbed is of the order of 0.13 at 50 °C and 0.3 at 95 °C. The presence of CO_2 can result only from secondary processes involving very unstable structures, for instance from a secondary hydroperoxide (Fig. 3).

Aldehydes are extremely reactive in radical processes; peracids are very unstable hydroperoxides and acyloxy radicals undergo decarboxylations at very high rates [10]. CO_2 (and acid) formation is thus governed by the slowest step, i.e. presumably the formation of the starting secondary hydroperoxide or its decomposition. With a mechanism of such complexity, it is not surprising to observe variations of the relative yields, such as CO_2/O_2 with temperature as found by Gillen et al. [6].

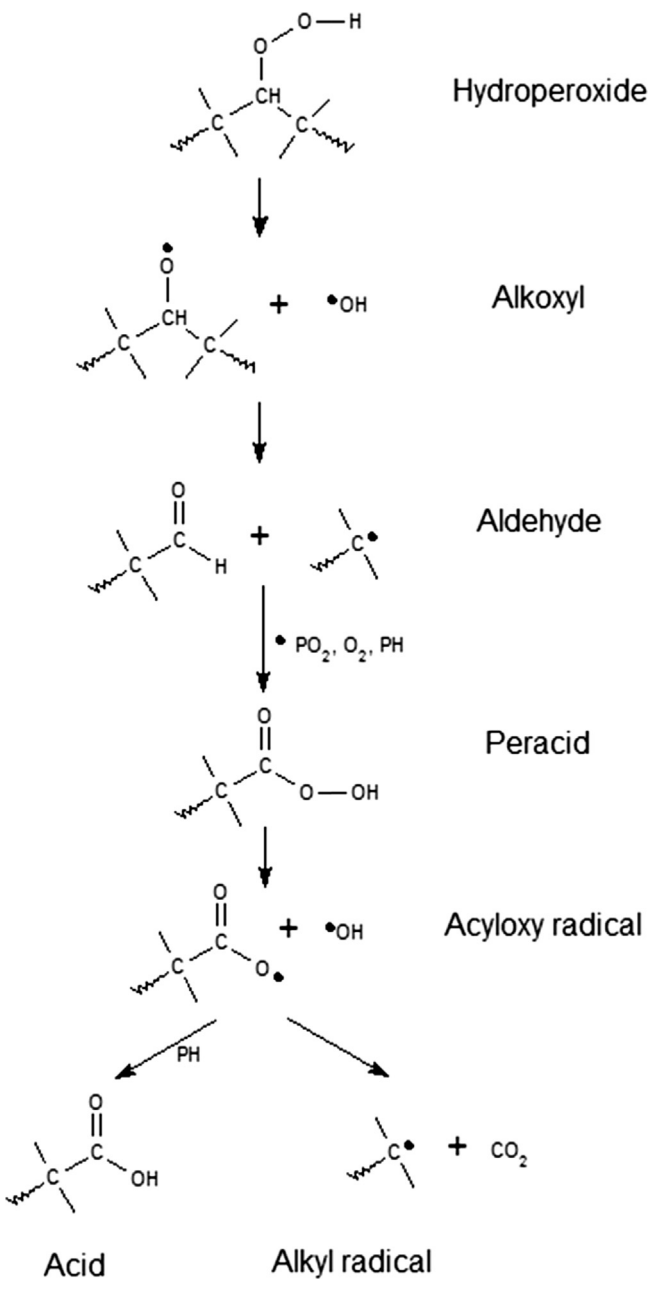

Fig. 3. Possible route for CO_2 formation.

The aim of this work is to complete the experimental data on lCR oxidation, especially by a study of the oxygen pressure effect on oxidation kinetics, by double bond IR titration, and by determination of the quantity of chlorine remaining linked to the polymer. A simplified kinetic model will be established to try to simulate these results.

This study aims to make a specific characterization of raw polychloroprene oxidation in different conditions in terms of temperature and oxygen pressure using a new ageing tool that allows in situ measurements. Based on both experimental results in this study and data available in literature, a mechanistic model of raw CR oxidation will be set up. Determination of the associated elementary rate constants and their temperature dependence will then be described. Finally, comparison of these rate constant values with those of other polydienic elastomers will be used in order to highlight specificities of raw CR oxidation.

2. Material and methods

2.1. Material

The sample considered here is a raw polychloroprene with a commercial reference of Baypren 116. The polymer density is equal to 1250 kg $m^{-3}$and weight average molar mass, assessed by GPC, is close to 140 kg/mol.

2.2. FTIR

The tool used in order to perform in situ chemical characterization during oxidation is an ageing chamber (Harrick TFC MXX-3 equipped with IR transparent windows) that can be controlled in both temperature (up to 240 °C) and atmosphere composition and pressure (up to 3 MPa). This ageing cell is placed in a Perkin Elmer Spectrum 2 Infrared spectrophotometer where the sample spectra were periodically collected. Each spectrum resulted from the averaging of 32 scans with a resolution of 4 cm^{-1}.

Polychloroprene was dissolved in chloroform and then a film is cast on a ZnSe window, residual solvent was dried out prior to ageing. Sample thickness was about 15 microns. Exact sample thickness was evaluated using the intensity of the band of double bonds situated at 1660 cm^{-1}, using the Beer—Lambert law with a molar absorptivity value of 25 l mol^{-1} cm^{-1} (calculated from Ref. [11]).

Concentrations of species under consideration were calculated using the Beer—Lambert equation with the molar absorptivity values listed in Table 1. For the determination of double bond concentration, a deconvolution was necessary owing to the overlapping of their band (which decreases) with the carbonyl one (which increases). Deconvolution is performed using the automatic software tool named Origin®, in fact the global peak situated between 2000 cm^{-1} and 1500 $cm^{-1}$is deconvoluted in three peaks situated at 1660 cm^{-1}, 1725 cm^{-1} and 1790 cm^{-1} respectively attributed to carbon—carbon double bonds, ketones and acid chlorides.

Table 1
Attribution of main infrared bands that evolves during CR oxidation.

Wave number (cm^{-1})	Evolution	Attribution	Reference	Molar absorptivity (l mol^{-1} cm^{-1})
1660	Decrease	C=C	[11–13]	25
1725	Increase	C=O in saturated ketone	[9, 12, 13]	320
1790	Increase	C=O in chlorine acid	[9, 12, 13]	300

2.3. Chlorine content

Sample thickness was chosen in order to avoid any limitation of degradation by O_2 diffusion, 100 microns thick samples of raw polychloroprene were aged in an oven at 80 °C. Chlorine content was measured using a potentiometric method using a DL50 device from Mettler, with an accuracy estimated around 0.6%.

3. Results

3.1. Molecular modifications

Examples of IR spectra are shown in Fig. 4. They display the same features as the spectra presented by Delor et al. [9]. The main changes are summarized in Table 1 with the assignments and the estimated values of the corresponding molar absorptivity values used to translate absorbance values into approximate concentrations. Special attention has to be paid to the modifications in the 1500–2000 cm^{-1}spectral region corresponding to carbonyls and double bonds (zoom in Fig. 4): In the spectral domain corresponding to the carbonyl stretching band (1680–1800 cm^{-1}) two peaks can be clearly distinguished: one at 1725 cm^{-1}, generally attributed to aliphatic, saturated ketones and the other at 1790 cm^{-1} attributed to acid chlorides. It is interesting to plot the ketone concentration against acid chloride concentration for all the exposure conditions under study (Fig. 5). It appears that, in the domain of moderate conversions, both concentrations are proportional irrespective of temperature or oxygen pressure, which leads to suppose that both species could have the same precursor and that their build-up kinetics could be closely linked to their formation rate.

From the quantitative analysis of IR spectra, it is possible to follow carbonyl build-up and double bond consumption during oxidation of raw CR. Fig. 6 shows an example of such evolution for a sample exposed to air at 80 °C. An increase in carbonyl content is observed during CR oxidation whereas a large decrease of double bond concentration occurs. These results clearly show that the consumption of double bonds cannot be neglected in a kinetic analysis.

The kinetic curves of Fig. 6 clearly show the absence of induction period that can result from hydroperoxide instability or from a high initial hydroperoxide concentration. Since the second hypothesis can be rejected, it can be concluded that the hydroperoxides

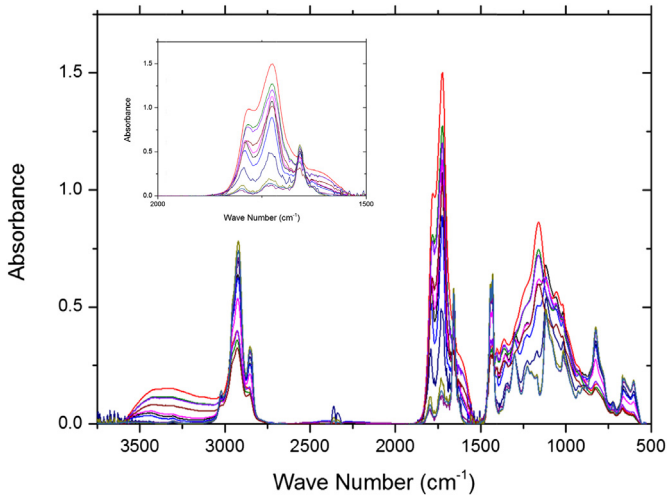

Fig. 4. Infra red spectra evolution during raw polychloroprene oxidation.

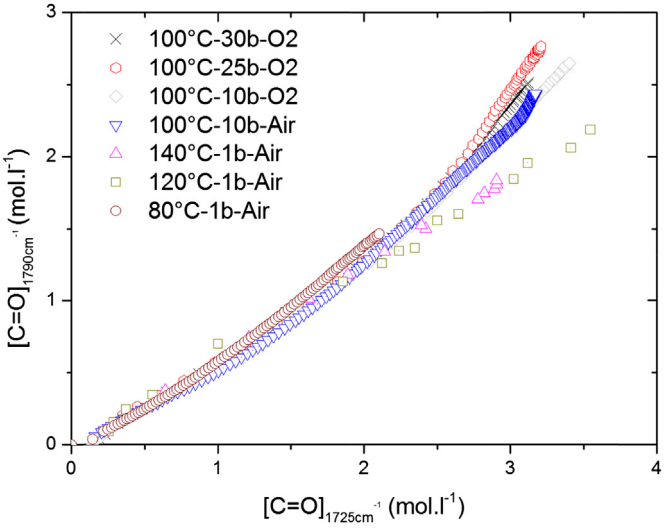

Fig. 5. Evolution of chloride acid concentration versus ketone concentration for different ageing conditions.

formed during lCR oxidation are particularly unstable. This is consistent with the hypothesis that α chlorohydroperoxides are formed.

Based on these results, is appears that polychloroprene stable oxidation products are essentially ketones and acid chlorides which are formed in closely related chemical events. Furthermore, double bond consumption is a major oxidation process and has to be considered in a mechanistic scheme. But one of the main questions when considering polychloroprene oxidation is the effect of chlorine on polymer oxidation.

3.2. Chlorine content

In order to evaluate this effect and more especially the possible formation of hydrogen chloride during oxidation, chlorine concentration in CR has been measured for different oxidation levels when exposed to air at 80 °C. Results are plotted in Fig. 7, where chlorine content is plotted as a function of acid chloride concentration. It appears that chlorine content does not decrease much, even for high oxidation level; this result is in accordance with previous observations made by Celina [7]. It has to be noted that a

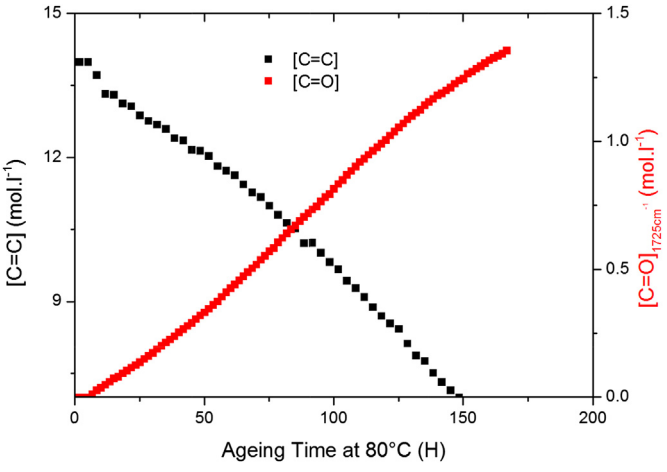

Fig. 6. Carbonyl build-up and double bond consumption during oxidation of raw CR in air at 80 °C.

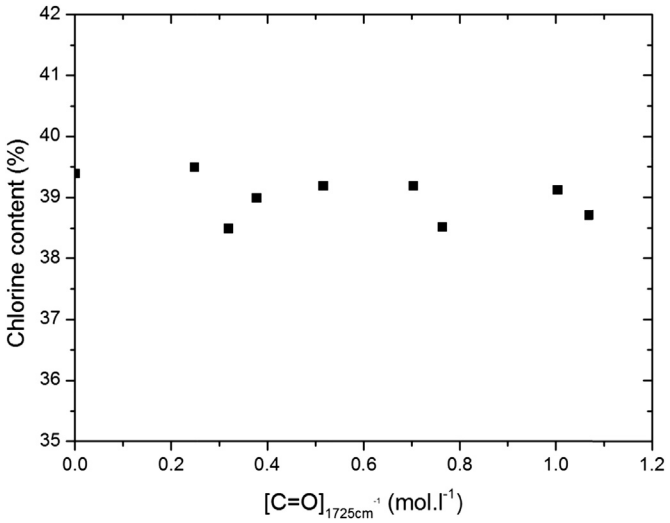

Fig. 7. Chlorine content versus carbonyl concentration during CR oxidation.

very small decrease could be suspected, this small decrease needs confirmation using more accurate experimental techniques and will not be considered here.

3.3. Effect of oxygen pressure

The effect of oxygen pressure on oxidation kinetics of raw polychloroprene has been considered at 100 °C, The curves of double bond depletion versus time are plotted in Fig. 8. These results clearly show that the higher oxygen pressure is, the faster double bonds are consumed, meaning that raw CR is not in an oxygen-excess regime in air at atmospheric pressure.

3.4. Effect of temperature

Obviously by increasing ageing temperature, oxidation rate is increased leading to a faster increase in carbonyl concentration (Fig. 9a) and faster double bond consumption (Fig. 9b). From these results, it appears that carbonyl build-up and double bond consumption occur in the same timescale at all temperatures.

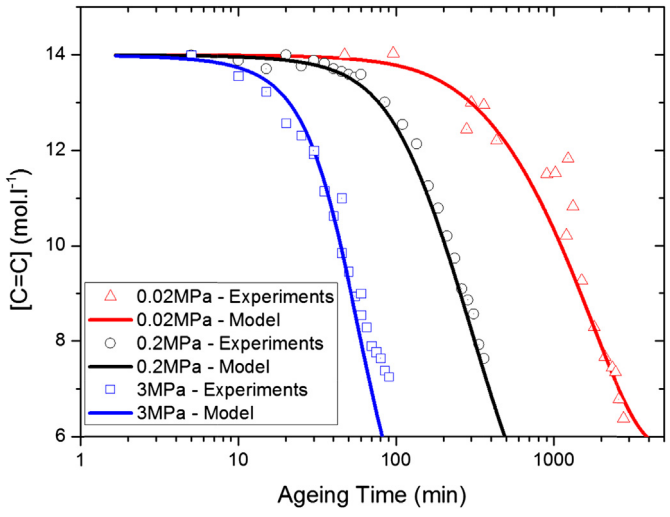

Fig. 8. Effect of oxygen pressure on carbon double bond consumption during CR oxidation.

The experimental part of this study highlighted the fact that polychloroprene oxidation begins rapidly and is characterized by a complex mechanism that presumably involves a double propagation process through peroxyl addition to double bonds and hydrogen abstraction by peroxyls. In the meantime, it appears that chlorine atoms remain bonded to the polymer; their splitting-off can be neglected. The next section will focus on the possibility to model this complex behaviour in order to set up a life time prediction scheme.

3.5. Oxidation kinetic modelling

This study aims to set up a mechanistic model of raw polychloroprene oxidation based on results from the literature presented in the Introduction and data presented in the previous section. The proposed mechanism can be considered as simply as possible taking into account all information available; it is based on the classical mechanistic scheme of oxidation to which radical addition to double bonds has been added and both unimolecular and bimolecular modes of hydroperoxide decomposition have been considered:

(1u) $POOH \rightarrow 2P^{\circ} + \gamma_1 \cdot C{=}O \quad (-4PH) \quad (k_{1u})$

(1b) $2POOH \rightarrow P^{\circ} + POO^{\circ} + \gamma 1 \cdot C{=}O \quad (-2PH)$

(2) $P^{\circ} + O_2 \rightarrow POO^{\circ} \quad (k_2)$

(3) $POO^{\circ} + PH \rightarrow POOH + P^{\circ} \quad (-2PH)$

(F1) $P^{\circ} + F \rightarrow P^{\circ} \quad (-PH) \quad (k_{f1})$

(F2) $POO^{\circ} + F \rightarrow P^{\circ} \quad (-2PH) \quad (k_{f2})$

(4) $P^{\circ} + P^{\circ} \rightarrow \text{inactive product} \, (k_4)$

(5) $P^{\circ} + POO^{\circ} \rightarrow \text{inactive product} + \gamma_1 \cdot POOH \quad (k_5)$

(6) $POO^{\circ} + POO^{\circ} \rightarrow \text{inactive product} + C{=}O \quad (k_6)$

The system of differential equations derived from this scheme (Appendix 1) is resolved with the following parameter values

$[P^{\circ}] = [POO^{\circ}] = 0 \text{ at } t = 0.$

$[POOH] = [POOH]_0 = 5 \cdot 10^{-3}$ mol L^{-1} at $t = 0$. This value does not result from a measurement but rather from the inverse approach (Appendix 1).

[PH] is the concentration of methylenes in allylic placement. Thus $[PH]_0 = 2\rho M_0^{-1} = 28$ mol L^{-1} where M_0 is the molar mass of the monomer unit (85 g mol^{-1}) and ρ is the polymer density (1250 g L^{-1}).

The equilibrium oxygen concentration has been estimated from the solubility coefficient value reported by Van Krevelen [14]: $S = 3 \cdot 10^{-8}$ mol L^{-1} Pa^{-1}, using Henry's law: $[O_2] = S \cdot p_{O_2}$ where p_{O_2} is the partial pressure of oxygen.

No stationary state hypothesis is made; substrate [PH] consumption is taken into account. At high conversions, secondary reactions can interfere with the above chain mechanism. To avoid such complications, simulations were stopped when the double bond concentration reached half of its initial value i.e. 7 mol L^{-1}.

The determination of elementary rate constants is based on the following approach: Propagation rate constants are extracted from

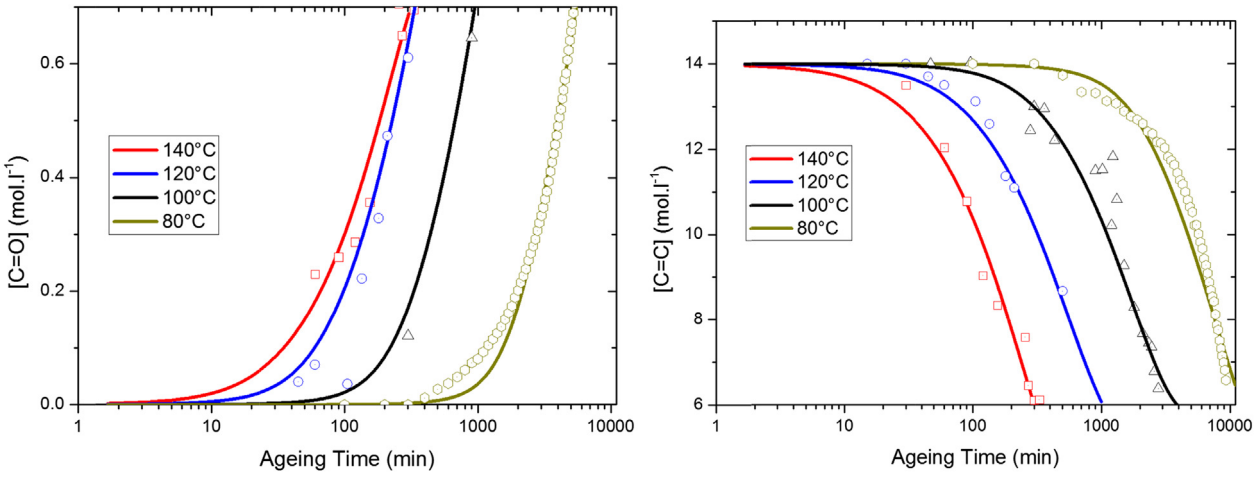

Fig. 9. Effect of temperature on carbonyl build-up and double bond consumption.

the literature: k_2 because it does not depend strongly on structure (when P° radicals are not too conjugated or hindered) and small variations of k_2 have a negligible effect on simulations. Here, we have chosen $k_2 = 10^8$ L mol^{-1} s^{-1}. It has been shown [15] that k_3 does not depend strongly on molecular mobility and is almost the same for polymers and their model compounds. For these latter, k_3 and its activation energy E_3 are sharply linked to the C—H dissociation energy D(P—H) and can be estimated using an empirical relationship [16].

$$\mathrm{Log}[k_3(30\ ^\circ\mathrm{C})] = 15.4 - 0.2 * \mathrm{D[P{-}H]} \quad (1)$$

$$E3 = 0.55 * (\mathrm{D[P{-}H]} - 62.5) \quad (2)$$

Where k_3 is expressed in l mol^{-1} s^{-1}, E_3 and D[P—H] in kcal mol^{-1}. In CR, D(PH) is equal to 87 kcal mol^{-1} [17].

Application of these relationships to the case of CR leads to:

$$k_3 = 4.4 \cdot 10^7 \exp(-56000/RT) \quad (3)$$

All the other rate constants have been determined from experimental data, using the kinetic scheme in an inverse approach. A two-steps procedure is used: in the oxygen-excess regime (see below), all the reactions involving radicals P° except O_2 addition can be neglected, the inverse approach gives access to initiation k_{1u} and/or k_{1b}, POO° addition to double bonds (k_{f2}) and POO° + POO° termination (k_6) rate constants. These values being known, one can determine the remaining rate constant values: k_{f1}, k_4 and k_5, applying the inverse approach to the results obtained in oxygen defect regime.

3.6. Effect of oxygen pressure

According to Fig. 8, the oxidation rate at 100 °C has reached its asymptotic value at the highest O_2 pressure values, so that it can be considered that oxidation occurs in an oxygen-excess regime at 3 MPa oxygen pressure. The determination of the corresponding rate constant values was then made. These values are listed in Table 2. The kinetic scheme was then used with these rate constant values to simulate the consumption of double bonds. The result of the simulation is shown in Fig. 10 together with the experimental curve, showing an acceptable agreement.

The whole kinetic scheme was then used to simulate oxidation in an oxygen deficient regime. The curves of double bond consumption at O_2 partial pressures of 0.2 and 0.02 MPa (this latter corresponding to air at atmospheric pressure) are also plotted in Fig. 8. Here again a good agreement between model and experimental data is observed.

In Fig. 10 the reciprocal rate of double bond consumption has been plotted against reciprocal O_2 pressure. When propagation occurs only by hydrogen abstraction, it has been demonstrated a long time ago [18] that under certain conditions (stationary state, no POOH decomposition, long kinetic chains, $k_5^2 = 4k_4k_6$) the dependence must be linear [19]. It has been shown many times, later, that this relationship remains linear even when the validity conditions are not obeyed, but this is the first time, to our knowledge that this relationship has been applied to a case of dual propagation, revealing its universality. The corresponding equation is:

$$r_{ox} = r_{ox\infty}\frac{\beta\cdot[O_2]}{1+\beta\cdot[O_2]} \quad \text{or} \quad \frac{1}{r_{ox}} = \frac{1}{r_{ox\infty}} + \frac{1}{r_{ox\infty}\cdot S\cdot\beta\cdot p_{O_2}} \quad (4)$$

It is possible to define approximately a critical pressure p_c, for instance:

$$p_c = \frac{1}{q\beta S} \quad (5)$$

q being an arbitrarily chosen number higher than unity, for instance $q = 10$.

This critical pressure separates arbitrarily the regime of oxygen deficient and the regime of oxygen-excess. Here this pressure is about 2 MPa i.e. a pressure about 100 times higher than the oxygen partial pressure in air at atmospheric pressure. It is clear that in the case of exposure in air, kinetic modeling must take into account terminations (4) and (5).

Table 2
Constant rates used for modelling oxidation at 100 °C.

	Polychloroprene	Polyisoprene	Polybutadiene
$[POOH]_0$ (mol l^{-1})	5.10^{-3}	5.10^{-2} to 5.10^{-3}	8.10^{-4} to 1.10^{-2}
k_{1u} (s^{-1})	3.10^{-4}		
k_{1b} (l mol^{-1} s^{-1})	1.10^{-3}	$6.2\cdot10^{-5}$	$1.6\ 10^{-6}$
γ_1	0.5	0.27	0.4
k_2 (l mol^{-1} s^{-1})	1.10^8	$1\cdot10^8$	1.10^9
k_3 (l mol^{-1} s^{-1})	0.65	8.4	1.5
k_{f1} (l mol^{-1} s^{-1})	500	$5.9\cdot10^4$	$1\ 10^4$
k_{f2} (l mol^{-1} s^{-1})	4.5	37	24
k_4 (l mol^{-1} s^{-1})	$1.7\cdot10^{11}$	$1\cdot10^9$	$3\ 10^8$
k_5 (l mol^{-1} s^{-1})	$1.7\cdot10^{10}$	$4.8\cdot10^8$	$1.2\ 10^8$
k_6 (l mol^{-1} s^{-1})	5.10^4	$6.6\cdot10^4$	$1\ 10^4$

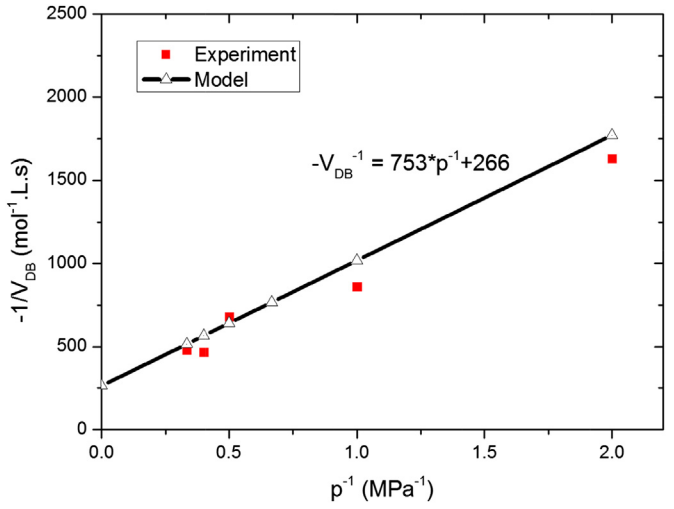

Fig. 10. Reciprocal of the double bond consumption rate against reciprocal of the oxygen pressure.

3.7. Physical meaning of rate constant values and their hierarchy

We have no rigorous proof that the set of rate constants resulting from the inverse determination is a unique solution of the problem. A check of their physical validity appears thus desirable. Let us first consider the hierarchy of values:

$k_4 > k_5 > k_2 >> k_6 >> k_3 >> k_{1b}$

And $k_2 > k_{f1} > k_{f2} > k_3$

These inequalities reflect several general rules:

i) If radicals are called R and non-radicals are called N, reaction rates are generally in the order: R + R > R + N > N + N. Transposed to the domain of polymer oxidative ageing: termination > propagation > initiation.
ii) Alkyl radicals are considerably more reactive than the corresponding peroxy radicals. This is valid for terminations ($k_4 > k_5 > k_6$). According to Gillen and Clough [20] for radical mobility reasons, one expects $k_5^2 > 4k_4k_6$ as observed here.
iii) Let us recall that O_2 is a biradical in ground state, in other words an O_2 addition on a radical can be also considered as a termination. O_2 would behave as a peroxyl but less reactive than a POO° so that: $k_5 > k_2 >> k_6$.
iv) Additions of peroxyls to double bonds are (slightly) faster than hydrogen abstractions to saturated groups as found for other polydienic polymers [21].
v) Hydroperoxide decomposition is, by far, the slowest elementary process that can be explained schematically by the fact that (in the domain of thermal reactions) radical creation is the most thermo-chemically disfavoured process. Concerning the mode of hydroperoxide decomposition, we know that at a given temperature, it is possible to define a critical hydroperoxide concentration $[POOH]_c = k_{1u}/k_{1B}$ at which both the unimolecular and the bimolecular POOH decomposition processes have equal rates. Here, $[POOH]_c = 0.3$ mol $L^{-1} >> [POOH]_0$ ($5 \cdot 10^{-3}$ mol L^{-1}). It can be deduced that oxidation begins in unimolecular mode and turns to bimolecular mode when [POOH] becomes equal to the critical value.

Table 3
Time for consumption of half of double bonds in several rubbers à 100 °C.

Nature of the rubber	Time to consume half double bonds at 100 °C (hours)
Polyisoprene	2
Polychloroprene	50
Polybutadiene	4
EPDM	150

3.8. Comparison of polychloroprene with other polydienes

From Table 2, it clearly appears that the initiation process is much faster in polychloroprene than in other polydiene rubbers, this difference could be attributed to the destabilizing effect of chlorine atoms on hydroperoxide decomposition. As a consequence, the induction period has almost completely disappeared in lCR while it is present in other polydienes. Despite its high initiation rate, CR displays a steady state rate lower than in other polydienes (Table 3) because all propagation processes are slower. That is also obviously due to the presence of chlorine, presumably through inductive effects.

3.9. Temperature effect

The effect of temperature on oxidation rate has been considered from 80 °C to 140 °C in air. Rate constant values have been adjusted for all tested temperatures separately and then temperature dependence has been considered; results of modelling are plotted in Fig. 9. It is worth nothing that temperature dependence of k_3 is fixed according to literature results (equations n°3 & 4) and temperature effects on k_2, k_4 and k_5 can be neglected. The Arrhenius parameters of the rate constants are given in Table 3.

Literature values of the activation energy of POOH decomposition [22] range between 80 and 140 kJ mol^{-1} meaning that the value in Table 3 is in accordance with previous results. However, if we compare this value with those of others polydienic elastomers it appears that the activation energy of the unimolecular decomposition of POOH is of the same order but lower. This is presumably due to the destabilizing effect of chlorine in α chlorohydroperoxides. The decreasing chlorine effect on the activation energy of unimolecular POOH decomposition process is such that it becomes almost equal to the bimolecular one. As a consequence, both decomposition processes participate in initiation at every temperature in the 80°C–140 °C interval (Table 4).

5. Conclusion

The thermal oxidation of unstabilized, uncrosslinked, unfilled polychloroprene has been studied in the 80–140 °C temperature interval in air at atmospheric pressure and in the 0.02–3 MPa pure oxygen pressure interval at 100 °C. Carbonyl (including acid chloride) build-up and double bond consumption were monitored by IR spectrophotometry. No significant chlorine release was observed. The discussion

Table 4
Temperature dependence of kinetic rates.

	Polychloroprene			Polyisoprene	Polybutadiene
	ko	Ea (KJ/mol)	R^2	Ea (KJ/mol)	Ea (KJ/mol)
K_{1u} (s^{-1})	$1.0 \cdot 10^{12}$	111	0.993	134	
K_{1b} (l mol^{-1} s^{-1})	$9.4 \cdot 10^{11}$	107	0.995	102	137
K_{f1} (l mol^{-1} s^{-1})	$2.1 \cdot 10^{7}$	33	0.996	11	0
K_{f2} (l mol^{-1} s^{-1})	$1.1 \cdot 10^{10}$	67	0.998	34	94
K_6 (l mol^{-1} s^{-1})	$9.0 \cdot 10^{12}$	59	0.966	23	71

of results was based on a mechanistic scheme mainly characterized by dual propagation (Hydrogen abstraction plus peroxyl addition to double bonds). Certain rate constant values (k_2 and k_3) were extracted from the literature, the other were determined from experimental results using the kinetic scheme in an inverse approach. Among the observations made on rate constant values, the following appear especially important: i) hydroperoxides are particularly unstable, that can be attributed to the presence of chlorine in α placement; ii) POO° addition on double bonds is significantly faster than hydrogen abstraction by POO°; iii) propagation is slower in polychloroprene than in other polydienes. This model of raw polychloroprene will now be adapted in order to be able to describe oxidation of vulcanized rubber and perform life time predictions.

Appendix

According to the mechanistic scheme, the following differential equation system can be written:

$$\frac{d[P^{\circ}]}{dt} = 2\cdot k_{1u}\cdot[POOH] + k_{1b}\cdot[POOH]^2 + k_3\cdot[PH]\cdot[POO^{\circ}] + k_{f2}\cdot[F]\cdot[POO^{\circ}] - k_2\cdot[P^{\circ}]\cdot[O_2] - 2\cdot k_4\cdot[P^{\circ}]^2 - k_5\cdot[P^{\circ}]\cdot[POO^{\circ}]$$

$$\frac{d[POOH]}{dt} = -k_{1u}\cdot[POOH] - 2\cdot k_{1b}\cdot[POOH]^2 + k_3\cdot[PH]\cdot[POO^{\circ}] + (1-\gamma_5)\cdot k_5\cdot[P^{\circ}]\cdot[POO^{\circ}]$$

$$\frac{d[POO^{\circ}]}{dt} = k_{1b}\cdot[POOH]^2 + k_2\cdot[P^{\circ}]\cdot[O_2] - k_3\cdot[PH]\cdot[POO^{\circ}] - k_{f2}\cdot[POO^{\circ}]\cdot[F] - k_5\cdot[P^{\circ}]\cdot[POO^{\circ}] - 2\cdot k_6\cdot[POO^{\circ}]^2$$

$$\frac{d[F]}{dt} = -k_{f1}\cdot[P^{\circ}]\cdot[F] - k_{f2}\cdot[F]\cdot[POO^{\circ}]$$

$$\frac{d[PH]}{dt} = -4\cdot k_{1u}\cdot[POOH] - 2\cdot k_{1b}\cdot[POOH]^2 - 2\cdot k_3\cdot[POO^{\circ}]\cdot[PH] - 2\cdot k_{f2}\cdot[POO^{\circ}]\cdot[F] - k_{f1}\cdot[P^{\circ}]\cdot[F]$$

$$\frac{d[C=O]}{dt} = \gamma_1\cdot k_{1u}\cdot[POOH] + \gamma_1\cdot k_{1b}\cdot[POOH]^2 + k_6\cdot[POO^{\circ}]^2$$

References

[1] Miyata Y, Atsumi M. J Polym Sci Polym Chem 1988;26:2561.
[2] Bailey HC. Rev Gen Caoutch Plast 1967;44(12):1495.
[3] Shelton JR, Pecsok RL, Koenig JL. Durability of Macromolecular materials. Am Chem Soc Wash 1979;chap 6:75.
[4] Cuccato D, Dossi M, Moscatelli D, Sorti G. Macromol Symp 2011;302:100.
[5] Colin X, Audouin L, Verdu J. Polym Degrad Stab 2007;92(5):886.
[6] Gillen KT, Bernstein R, Derzon DT. Polym Degrad Stab 2005;87:57.
[7] Celina M, Wise J, Ottesen DK, Gillen KT, Clough RL. Polym Degrad Stab 2000;68(2):171.
[8] Khelidj N, Colin X, Audouin L, Verdu J, Monchy-Leroy C, Pronier V. Polym Degrad Stab 2006;91:1598.
[9] Delor F, Lacoste J, Lemaire J, Barrois-Oudin N, Cardinet C. Polym Degrad Stab 1996;53:361.
[10] Fraind A, Tumcliff R, Fox T, Sodano J, Ryzhkov LR. J Phys Org Chem 2011;24(5):809.
[11] Coquillat M. Vieillissement des propergols a matrice polybutadiene. Arts et Métiers ParisTech; 2007, p. 65.
[12] Socrates G. Chichester: Infrared and Raman characteristic group frequencies Wiley; 2001.
[13] Arjunan V, Subramanian S, Mohan S. Turkish J Chem 2003;27(4).
[14] Van Krevelen DW, Te Nijenhuis K., Porperties of Polymers, Elsevier; 2009. p. 660.
[15] Mayo FR. Macromolecules 1978;11(5):942–6.
[16] Korcek S, Chenier JHB, Howard JA, Ingold KU. Can J Chem 1972;50:2285.
[17] Bendon SW. Thermochemical kinetics. 2nd ed. New York: John Wiley & Sons; 1986. p. 309.
[18] Bolland JL, Gee G. Trans Faraday Soc 1946;42:236.
[19] Bolland JL. Q Rev Chem Soc 1949;3(1):1–21.
[20] Wise J, Gillen KT, Clough RL. Polymer 1997;38(8):1929.
[21] Howard JA. Can J Chem 1972;50(14):2298.
[22] Ingold KU. Chem Rev 1961;61(6):563.